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(54) **Process for preparing organic hydroperoxides**

(57) The invention relates to a process for preparing organic hydroperoxides by oxidation of a hydrocarbon feed with molecular oxygen at supercritical conditions, which process is carried out in the presence of a separate liquid water phase that is present in an amount of 0.5 to 20% weight on the weight of the feed as a water film on the inner walls of the reactor vessel.

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## Description

### Background of the Invention

[0001] The invention relates to a process for preparing organic hydroperoxides.

[0002] Processes for the preparation of organic hydroperoxides by oxidising the corresponding hydrocarbons are known from US patents Nos. 4,329,514; 4,404,406; 4,408,081; 4,408;082; European patents applications Nos. 584,956 and 567,336 and other documents. Tertiary-butyl hydroperoxide (TBHP) may be prepared this way, as well as hydroperoxides of cyclohexane, cumene and ethylbenzene. TBHP is of particular interest, as it can be used in the synthesis of propylene oxide (PO) and, via the intermediate tertiary butyl alcohol, of methyl tertiary-butyl ether (MTBE). An example of this synthesis is found in European patent application No. 416,744 and prior art discussed therein.

[0003] The synthesis of organic hydroperoxides is not an easy one. Aside from (explosive) runaway reactions, also the lack of selectivity towards the desired organic hydroperoxide is an issue of major concern. A 100 percent yield is impossible due to the variety of oxidation reactions competing with each other. Besides, the yield is also affected by decomposition of the hydroperoxide. For instance, cumene hydroperoxide will decompose (rearrange) into phenol and acetone (cf. "Organic Chemistry" by Morrison and Boyd, 3rd ed., sec. 28.6). Similar reactions are known from "Advanced Organic Chemistry" by Jerry March, 3rd ed. (cf. reaction 8-23). This decomposition may be catalysed by trace amounts of metal ions derived from the (chromium/steel) inner reactor walls (e.g., $Fe2+$ and $Fe3+$).

[0004] The first step as described in the art to improve the selectivity and reduce decomposition concerns treatment of the reactor walls, typically with sodium pyrophosphates as disclosed in US patent No. 3,816,540, or with sodium stannate. Often the inner reactor walls are already passivated by the manufacturer prior to delivery. This method is effective, as removing the sodium pyrophosphates lowers the selectivity, which may be restored upon renewed passivation.

[0005] Another approach concerns the use of reactors that are entirely inert, such as, gold plated reactors. Increased selectivity's under comparable circumstances may be found. However, the prevailing reaction conditions will damage the gold plating, resulting in the loss of selectivity. As the manufacture and rejuvenation of gold plated reactors is highly expensive, this approach is not attractive.

[0006] Ideally the selectivity towards organic hydroperoxides is improved up to the rate achievable in a gold plated reactor, without the disadvantages mentioned above. This the inventors now have achieved with a relatively simple adaptation of known processes.

### Summary of the Invention

[0007] The invention provides a process for preparing organic hydroperoxides by oxidation of a hydrocarbon feed with molecular oxygen at supercritical conditions, which process is carried out in the presence of a separate liquid water phase that is present in an amount of 0.5 to 20% weight on the weight of the feed as a water film on the inner walls of the reactor vessel.

### Detailed Description of the Invention

[0008] The inventors found plain water to be able to shield the reactor walls, thereby preventing contact between the organic hydroperoxides and the reactor walls. Surprisingly, the decomposition is not brought about by metal ions transmigrating through the water film. Moreover, water and (Lewis) acids are known to catalyse the rearrangement of the organic hydroperoxides, which would have caused the skilled reader to believe more rather than less decomposition to occur.

[0009] Preferably, the water is present in an amount of 0.75 to 10% w/w, more preferably in an amount of 1.0 to 3.0% w/w.

[0010] The preservation of the water film depends on the geometry of the reaction vessel and the manner (rate) of stirring, and it may be affected by addition of water during the process. The proper form and location of the rotor blades as well as manner of stirring may be determined without difficulty in a limited number of experiments or through suitable computer design.

[0011] A further important variable is the density of the reaction mixture. For instance, the density of TBHP is lower than that of ethylbenzene hydroperoxide, making it easier to form a stable film to shield the inner reactor walls. The density of the reaction mixture may of course be varied through the use of solvents.

[0012] Contrary to passivation, the effect of enhanced selectivity does not continue indefinitely. If in the process the water film deteriorates due to water loss, as may occur in continuous reactions, then the water should be replenished. If not, a decrease in selectivity comparable to that of unpassivated reactor vessels may occur.

[0013] Moreover, mere addition of water does not suffice. If it does not form the separate phase that shields the inner reactor walls the outcome of the process will be quite different. For instance, European patent application No. 399,776, describes the production of acetophenone which is the decomposition product of ethylbenzene peroxide. In that production process the (direct) water addition rather increases the selectivity in favour of the decomposition product. The reason for this difference in behaviour is likely caused by water dissolution in the product phase (at too low concentrations) and/or insufficient shielding of the inner reaction walls (at too high or too low stirrer speed, and/or too small a difference in density).

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Example 5

[0027] In this example the stirrer speed and direction have been varied. In absence of water, the stirrer speed does not influence the selectivity. However, in the presence of 3% w/w water, the TBHP/TBA ratio (w/w) increased from 2.8 to 3.6 with a stirrer speed going from 330 to 1180 rpm. At 330 rpm, the stirring direction also influences the TBHP/TBA ratio, but this is not the case at 1180 rpm. These experiments illustrate the importance of proper stirring conditions to achieve optimal selectivity.

**Claims**

1. A process for preparing organic hydroperoxides by oxidation of a hydrocarbon feed with molecular oxygen at supercritical conditions, which process is carried out in the presence of a separate liquid water phase that is present in an amount of 0.5 to 20% weight on the weight of the feed as a water film on the inner walls of the reactor vessel.

2. A process as claimed in claim 1, wherein the water is present in an amount of 0.75 to 10% w/w.

3. A process as claimed in claim 1, wherein the water is present in an amount of 1.0 to 3.0% w/w.

4. A process as claimed in any one of claims 1 to 3, wherein the hydrocarbon feed comprises isobutane or isopentane.

5. A process as claimed in any one of claims 1 to 4, carried out at a pressure in the range of 2 to 100 bar, preferably in the range of 10 to 90 bar, more preferably in the range of 30 to 80 bar.

6. A process as claimed in any one of claims 1 to 5, carried out at a temperature in the range of 125 to 175 °C, preferably 145 to 160 °C.

7. A process as claimed in any one of claims 1 to 6, wherein the hydrocarbon feed is isobutane, and a pressure in excess of 36 bar and a temperature in excess of 135 °C is used.

8. A process as claimed in any one of claims 1 to 7, wherein the conversion of the hydrocarbon feed is 1 to 25%, based on the hydrocarbon feed.

9. A process as claimed in any one of claims 1 to 8, wherein the amount of oxygen is 10 to 20 % mole on mole of the hydrocarbon feed.